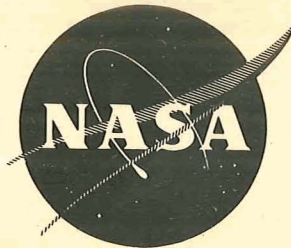


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THE DEVELOPMENT OF PRECIPITATION-HARDENED  
CHROMIUM-BASE ALLOYS

by

E. A. Brandes and B. A. Hatt

FULMER RESEARCH INSTITUTE LIMITED

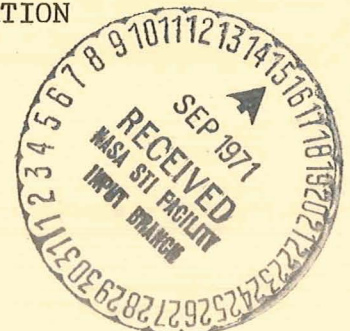
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NASA Lewis Research Center

Contract NASw-1720

William D. Klopp, Project Manager



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FINAL REPORT

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CHROMIUM-BASE ALLOYS

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E. A. Brandes and B. A. Hatt

FULMER RESEARCH INSTITUTE LIMITED

Stoke Poges

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

March 24, 1971

Contract NASw-1720

NASA Lewis Research Center

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## FOREWORD

The research described herein, which was conducted by the Fulmer Research Institute Ltd., was performed under NASA Contract NASA CR-72874. The work was done under the management of NASA Project Officers J. Merutka and W.D. Klopp. The work was originally issued as Fulmer Research Institute Report - R.304.

### ABSTRACT

An exploration of chromium based alloys, precipitation hardened by means of intermetallic compounds formed between Zr-Si, Ti-Si and Ti-Be failed to produce useful materials.

Strong creep resistant alloys were found in the systems Cr-Ti-C and Cr-Cb-C and Cr-Ta-C. The Cr-Ti-B and Cr-Cb-B systems were less promising because of  $\text{Cr}_4\text{B}$  formation.

## 1. SUMMARY

The objective of the research has been to produce a tough, dispersion-hardened chromium-base alloy with high strength at elevated temperatures and high ductility at ambient temperature. Since most solutes raise the temperature of the ductile/brittle transition in chromium, alloying systems have been sought in which the solutes can be precipitated as a fine dispersion of intermetallic compound in a matrix which is virtually pure chromium of low ductile/brittle transition temperature.

The elements should form intermetallic compounds of high enthalpy with each other but compounds of low enthalpy with chromium. Such compounds should have a moderate solubility in chromium at elevated temperature but near zero solubility at low temperatures. An examination of phase diagrams indicated that the following pairs of elements should fulfil these conditions.

- (i) Zirconium plus silicon or beryllium.
- (ii) Titanium plus silicon or beryllium.

A series of alloys, containing 1% and 5% by volume of the putative intermetallic compounds in these four systems, have been prepared but in no case did the chromium-free intermetallic compound come into equilibrium with the chromium solid solution; consequently one of the elements added remained in solid solution in chromium and thus would raise the temperature of the ductile to brittle transition. This phase of the work was terminated at this stage.

The second phase of the research was directed to the development of similar alloys in which hardening was caused by the precipitation of a carbide or boride of refractory metals. Alloys with attractive high temperature strengths were obtained by precipitation of the carbides of tantalum, columbium and titanium.

The alloys containing columbium and tantalum were produced in the as-rolled condition with ductile to brittle transition temperature between 122°F (50°C) and 216°F (102°C). By heat treatment the transition temperature of these alloys could be reduced to below 122°F (50°C). The best combination of properties was found in an alloy containing 2.33 wt % tantalum plus 0.12 wt % carbon. This alloy was ductile in tension at 215°F (102°C) and when heated to 2100°F (1149°C) had a 0.2% yield strength of 12.8 tonf/in<sup>2</sup> (198 MN/m<sup>2</sup>). In creep rupture tests at the same temperature, the stress to give a rupture life of 100 hours was 5.2 tonf/in<sup>2</sup> (80 MN/m<sup>2</sup>).

The substitution of boron in alloys containing titanium or columbium caused the precipitation of a chromium boride ( $\text{Cr}_4\text{B}$ ) and not the anticipated titanium or columbium borides. Thus such alloys would contain titanium or columbium in solid solution and would not be expected to have low ductile/brittle transition temperatures.

The general conclusion from this research is that the successful development of a tough, heat-resistant chromium-base alloy will be most likely realised by using the precipitation of refractory metal carbides and it is recommended that further consideration should be given to this aspect of the research.

## 2. INTRODUCTION

The objective of this work has been to develop a chromium-base alloy with the following three attributes:-

- (i) High strength and creep resistance at temperatures in excess of  $1,900^{\circ}\text{F}$  ( $1,038^{\circ}\text{C}$ ).
- (ii) A ductile/brittle transition temperature below ambient temperature.
- (iii) Resistant to embrittlement by nitridation at elevated temperature.

Such an alloy would be of potential value in high temperature engine applications. The work described in this report has concentrated on the first two of these objectives.

Attempts to improve the high temperature strength and creep resistance of chromium by solid solution hardening, has always caused loss of low temperature ductility by raising the temperature of the ductile/brittle transition. Therefore it was decided that high temperature strength in chromium alloys could best be provided by a fine dispersion of particles of an intermetallic phase of high stability precipitated in a matrix of substantially pure chromium so that its ductile/brittle transition temperature would be low. Three kinds of dispersed phase have been considered for this strengthening process:-

- (i) Precipitate of an intermetallic compound which contains no chromium. The elements in this compound should form no compound with chromium or, if this is impossible, should form compounds of low enthalpy. The two elements should form one or more metallic compounds with each other of high enthalpy which can come into equilibrium with the chromium solid solution and which has a moderate solubility at elevated temperatures i.e. just below the melting point of the alloy and an extremely low solubility at some lower temperature at which the alloy would be used in service.
- (ii) A precipitate of a compound between a refractory metal and an interstitial element such as carbon or boron. The choice of the refractory metal should be made on the same basis as in (i) above.
- (iii) A dispersion of a non-metallic compound like magnesium oxide.

The contract under which this research has been carried out was originally intended to cover development of alloys under mechanisms (i) above. Attempts to find intermetallic compounds which would precipitate in the manner proposed was unsuccessful and it was for this reason that this stage was terminated and the work extended to include a study of the precipitation of the carbides and the borides of the refractory metals, titanium, columbium and tantalum.

Three alloys containing carbon were sufficiently promising for large casts to be made which were extruded to provide material for tensile tests and creep tests at elevated temperatures. The most satisfactory creep resistance and tensile strength were found in chromium alloys strengthened by tantalum carbide.

The work carried out on the alloys containing boron was unsuccessful in that the only boride precipitated was chromium boride. Only two alloys containing boron were examined but time did not allow further investigation of other compositions containing different refractory metals.

The general policy in this research has been to carry out preliminary assessment of a wide range of alloys using 60 gram argon arc melted casts. This assessment was based largely on hardness tests and structural examination of the alloys. Promising alloys were then examined in detail; these were consumably argon arc melted and cast as  $2\frac{1}{8}$ " (5.4 cm) dia billets weighing approximately 2.75 kg (6 lbs). These were then extruded to half inch diameter and rolled to approximately  $\frac{1}{4}$ " (0.64 cm) diameter. The experimental details of the manufacture and fabrication of these alloys and the experimental techniques used are described in detail in an appendix to this report.

### 3. ASSESSMENT OF ALLOYS HARDENED BY THE PRECIPITATION OF INTERMETALLIC COMPOUNDS

#### 3.1. General Considerations

The alloy systems selected for study were as follows:-

- (i) Chromium-titanium-silicon in which the precipitate should be  $Ti_5Si_3$ .
- (ii) Chromium-titanium-beryllium in which the precipitate should be  $TiBe_{12}$ .
- (iii) Chromium-zirconium-silicon in which the precipitate should be  $Zr_2Si$ .
- (iv) Chromium-zirconium-beryllium in which the precipitating phase should be  $Zr_2Be_{17}$ .

The initial phase of the study was to assess firstly whether in fact the proposed intermetallic compounds could be precipitated from chromium to leave a chromium matrix which was substantially free from substitutional elements and, secondly, whether the ternary compound formed and whether this could be used to produce a satisfactory precipitation hardening system. In the first instance, the alloys were chosen from each system with compositions which would be expected to precipitate one volume percent and five volume percent of the expected compound if it had zero solubility in chromium.

Small buttons of these alloys were argon arc melted and cast and their general structure was determined. From this heat treatments were devised to ascertain whether precipitation hardening was possible in these systems.

### 3.2. Chromium-Titanium-Silicon Systems

Three alloys were examined from this system; two had compositions which should have produced one and five volume percent of  $Ti_5Si_3$  and the third had excess silicon over that required for five volume percent of the compound.

The results of the work on these alloys (AA384, AA383, AA391) are presented in Table 1 and the results are summarised in Table 2. All three alloys appeared to consist of a solid solution with the exception of a few pink particles, the presence of which did not appear to depend on composition or heat treatment. The hardness of the alloys appeared to depend on composition and did not change significantly on heat treatment. The lack of response to heat treatment indicated that the alloys all fell within the solid solution field even at the heat treatment temperature. Whilst it would be possible to introduce precipitation hardening by further increase in the titanium silicon concentration, this would only result in a precipitation-hardened alloy containing a matrix of high titanium and/or silicon content and would therefore be expected to have a high transition temperature. It was therefore decided that this system would not fulfil the original requirements proposed for an alloy of high strength and ductility and no further work has been carried out on it.

### 3.3. Chromium-Titanium-Beryllium Alloy

In the first instance two alloys have been melted and cast: one intended to produce one volume percent and the other to produce two volume percent of the compound  $TiBe_{12}$ . Results are summarised in Tables 1 and 2. The more dilute alloy had constant hardness irrespective of heat treatment and it is probable that this alloy remained a solid solution. Increasing the amount of titanium and beryllium caused a very significant rise in hardness to 460 Hv10\* in the as-cast state; ageing at 2,550°F (1,400°C) caused a further increase in hardness to 510 Hv10.

Metallographic examination showed that in the as-cast state there was some coring. On heat treatment at temperatures in the range 2,100°F (1,150°C) to 2,550°F (1,400°C), further precipitation of intermetallic compound occurred although this was concentrated in the inter-dendritic region. It was necessary to heat treat at 2,730°F (1,500°C) before this coring was removed (Figure 5).

\* Here and subsequently Vickers Pyramid Hardness  
No 10 kg load is indicated by Hv10.

This system was considered to be sufficiently promising to justify some examination of the effect of the beryllium-titanium ratio on the degree of precipitation. Therefore two series of alloys were cast; one containing 0.5 wt % titanium (0.54 atomic %) with up to 1.31 wt % beryllium (7.1 atomic %) and the second series containing 1.48 wt% titanium (1.6 atomic %) with up to 0.75 wt % (4.17 atomic %) beryllium. These alloys were both examined in the as-cast condition and after heat treatment for 15 hours at 2,280°F (1,250°C).

As can be seen from Figure 1, the hardness of the as-cast alloys increased almost linearly with the beryllium content; the higher titanium level caused an additional increase in hardness of approximately 40 Hv10. Heat treatment at 2,280°F (1,250°C) allowed softening to occur in alloys from the low titanium series with more than 3.2 atomic % beryllium and in alloys from the high titanium series with more than 2.5 atomic % beryllium. This suggests that these compositions represent the limit of solubility of titanium and beryllium in chromium at this temperature. These beryllium solubilities are only slightly less than the maximum solubility of beryllium in chromium at this temperature which is approximately 4 atomic percent. Since the solubility of titanium in chromium at this temperature is approximately 43 atomic percent, it is probable that the precipitate occurring in the ternary alloys is based on  $\text{CrBe}_2$  and not the anticipated  $\text{TiBe}_{12}$  precipitate. The consequence of this is that precipitation will not remove titanium from solid solution in the chromium and it is highly likely that alloys in this system will contain appreciable amounts of beryllium and titanium in solid solution after precipitation.

Whilst it is true that lower temperatures would reduce the solubility of beryllium and titanium and increase the amount of  $\text{CrBe}_2$  precipitate, it is unlikely that an alloy with a low ductile/brittle temperature would be produced; therefore no further investigation of this system has been carried out.

#### 3.4. Chromium-Zirconium-Silicon System

Two alloys were cast containing one and five volume percent of the putative  $\text{Zr}_2\text{Si}$  phase. The second phase in the eutectic was extracted electrolytically and the residue analysed; this showed that it contained 35% chromium 51% zirconium and 3% silicon. X-ray analysis of this residue detected  $\text{ZrO}_2$  plus another phase which could not be identified. It was certainly not  $\text{Zr}_2\text{Si}$  or  $\text{ZrCr}_2$  and it is therefore thought to be a ternary compound probably of composition approximately  $\text{Cr}_6\text{Zr}_3\text{Si}$ .

Heat treatments were carried out on both alloys as detailed in Table 1 but it was shown that the compound did not dissolve in the matrix at high temperature nor was it reprecipitated by heat treatment at lower temperature (Figure 6). Therefore, it was concluded that this compound was unlikely to be an effective precipitation hardener and work on this system ceased.



### 3.5. Chromium-Zirconium-Beryllium System

The first two alloys cast containing 1% and 5% of the putative  $\text{Zr}_2\text{Be}_{17}$  phase contained appreciable quantities of an intergranular and interdendritic degenerate eutectic. Heat treatment coarsened this eutectic (Figure 7) and caused appreciable precipitation within the grains. This suggested that this system was precipitation hardenable but that the amount of zirconium added was too high.

The amount of precipitate in this system indicated that the published solubility data for zirconium in beryllium were in error. Hanson<sup>(1)</sup> quotes the solubility as less than 1.5 atomic % zirconium and Domagala<sup>(2)</sup> as less than 0.6 atomic % zirconium. The evidence from the alloys examined in both the chromium-zirconium-silicon system and the chromium-zirconium-beryllium systems suggest that the solubility is appreciably less than either of these figures. Therefore a series of binary chromium-zirconium alloys were cast containing 0.04, 0.10, 0.19, 0.34 and 0.66 atomic percent zirconium. These showed that only the first two alloys were single phase in the as-cast condition or after annealing at temperatures down to 2,280°F (1,250°C). Therefore, the solubility limit for zirconium in chromium is estimated to be between 0.1 and 0.19 atomic percent.

Therefore, a new series of ternary chromium-beryllium alloys were cast which contained 0.095 atomic percent zirconium with beryllium contents of 0.19, 0.47, 0.95 and 4.58 atomic percent. These have been examined, as-cast and after annealing at 2,280°F (1,250°C) and the hardness results are shown in Figure 2. No eutectic was observed in the as-cast condition except in the alloy with the beryllium content of 4.58 atomic percent. Ageing produced precipitation in most of the alloys and the amount increased with beryllium content.

There was evidence that an alloy containing 0.095 atomic percent zirconium would have a maximum solubility for beryllium of one atomic percent. Despite the fact that the hardness level attainable appeared to be no greater than 200 Hv10, it was considered that this alloy system provided the best chance of fulfilling the original objective of precipitating an intermetallic compound in a matrix with a low solid solubility and it was decided that further work on this system was warranted.

### 3.6. Development of Specific Chromium-Zirconium-Beryllium Alloys

#### 3.6.1. Manufacture

Two chromium-0.12 atomic percent zirconium alloys were prepared for further development, containing 0.94 and 2.33 atomic percent beryllium respectively. These were cast as 2.75 Kg ingots by consumable electrode arc melting and casting. After machining to 2½" (5.4 cm) diameter bar, they were extruded to ½" (1.3 cm) diameter bar after preheating 2,530°F (1,400°C). Samples of the extruded bars were examined in the extruded condition and

after annealing at 2,280°F (1,250°C). A fine precipitate was visible in both alloys but there was no evidence that annealing produced additional precipitation - see Table 3. Lengths of each extrusion were sheathed in one inch diameter mild steel cylinders and were preheated to 2,120°F (1,160°C) from which they were rolled to 0.5" sq. section. After removing the sheath this produced chromium alloy bar of approximately 0.25" diameter; all specimens appeared to be free from cracks.

Attempts were then made to roll these quarter inch bars to strip suitable for the manufacture of bend test specimens. Two procedures were tried: firstly, hot rolling in the sheath and secondly, removing the sheath and preheating in a salt bath at 750-850°C and then rolling in air. Neither method was successful mainly because of the rapid chilling of the sample by the rolls. One sample of the more dilute alloy only was rolled successfully to 0.047" thick from a salt bath at 850°C using approximately 3% reduction per pass; attempts to repeat this on other samples were not successful.

### 3.6.2. Structural Examination

The structures of the worked alloys were examined by X-ray diffraction techniques. From Table 4 it can be seen that all rolled and extruded samples had a strong preferred orientation with  $\langle 110 \rangle$  directions along the working direction and that subsequent heat-treatments at 2,280°F (1,250°C) did not change this texture.

X-ray determination of the lattice parameter of the chromium solid solutions of these two alloys is illustrated in Figure 3 and is compared with the lattice parameter v. composition curve for chromium-beryllium alloys obtained by Johnston and Edward.<sup>(3)</sup> The lattice parameters obtained for the two alloys under examination correspond to 0.9 at % and 3.3 at % beryllium respectively assuming that all the zirconium is precipitated.

Four weak diffractions were observed in addition to the chromium diffraction from the low beryllium alloy. These extra diffractions could be indexed on a face centred cubic structure with a  $a$  approximately equal to 4.61Å; this indicated a mixed solid solution of ZrO, ZrC and ZrN. The lattice parameter of the chromium matrix was 2.883Å which is in good agreement with Johnston and Edward's value for a 0.9 at % beryllium alloy.

In the higher beryllium alloy, there were three additional diffractions not present in the dilute alloy. These had  $d$  values of 2.56, 2.18 and 1.82Å and intensities in the ratio 1:2:1. These can be explained by the simultaneous presence of ZrCr<sub>2</sub> and ZrBe<sub>2</sub> but not by any of the known zirconium-beryllium intermetallic compounds. The matrix had a lattice parameter of 2.8785Å which agreed well with Johnston and Edward's value for a composition of chromium-3.3 atomic percent beryllium. This is a lower parameter than would be expected from an alloy of the 2.3 atomic percent beryllium added and suggests some segregation in the alloy.

### 3.6.3. Bend Tests

Bend tests were made on specimens prepared from the rolled strip of the low beryllium alloy. These were first annealed for 15 hours at 2,280°F (1,250°C) to produce a recrystallised structure; they were subsequently electropolished before testing.

The results (Table 5) indicate a ductile/brittle transition temperature of approximately 572°F (300°C).

### 3.6.4. Conclusion

This more detailed investigation of the chromium-zirconium-beryllium alloys has shown that, although there was evidence of precipitation of an intermetallic compound, it was most probable that this is  $ZrCr_2$  and  $CrBe_2$ ; in other words, there was no precipitation of compounds from the Zr-Be system. The results have also shown that most of the beryllium remained in solution in the chromium; this was confirmed by the results of the bend tests which showed that the transition temperature was approximately 572°F (300°C). Abrahamson and Grant<sup>(4)</sup> have shown that the transition temperature of chromium is increased by beryllium additions especially when they exceed 1 atomic percent.

Thus this work shows that an alloy satisfying the original objectives outlined in the introduction cannot be obtained from the chromium-zirconium-beryllium system. Whilst lower temperatures of heat treatment may bring about denser precipitation, leaving a matrix of lower solute content, it must be remembered that a successful alloy will be subjected to operating temperatures in the region of 1,900°F (1,038°C) to 2,100°F (1,149°C). Therefore the criterion must be satisfied in alloys which have been heat treated at temperatures up to 2,280°F (1,250°C). For this reason, no further work on this system has been carried out.

## 4. ASSESSMENT OF ALLOYS HARDENED BY PRECIPITATION OF CARBIDES AND BORIDES OF THE REFRACTORY METALS

### 4.1. General Introduction

It is already known that chromium alloys containing fine dispersions of carbides formed with the refractory metals of groups IV and V of the Periodic Table, have excellent high temperature strengths, and good ductility. Many of these alloys are strengthened by a dispersion of tantalum carbide, one of which is an alloy containing 2% tantalum, 0.1% carbon and 0.05% yttrium which has been developed in Australia. Chromium has also been strengthened by the addition of the refractory metals from groups IV and V

to alloys containing boron. (7,8,9) By analogy with the alloys containing carbon, it has been postulated that the strengthening is due to the precipitation of a refractory metal boride; however, no detailed structural work has been carried out to confirm this nor has the boride been identified.

The experimental programme has been modified so that a comparison can be made between the high temperature strength and the ductility of chromium alloys containing approximately one volume percent of the carbide or boride of titanium or columbium. The properties of these alloys have been compared with a chromium alloy containing approximately 2% tantalum and 0.1% carbon, which was already available.

The experimental approach was to prepare a range of alloys in the form of small argon arc melted buttons and to determine the precipitation behaviour of these alloys and the approximate transition temperatures. These results were then used to select compositions for casting and fabrication on a larger scale for a more detailed investigation, including an assessment of their high temperature strength and creep resistance.

It has been shown that fine dispersions of refractory metal carbides are produced in alloys containing equal atomic proportions of the refractory metals and carbon but usually excess of the metal is required to prevent the formation of the chromium carbide,  $\text{Cr}_{23}\text{C}_6$ , during casting. Since a necessary condition for producing good low temperature ductility is that the precipitates should be dispersed in a relatively pure matrix, the alloys containing titanium and columbium carbides have been prepared with equal atomic proportion of refractory metal and carbon and also with slight excess of either carbon or the refractory metal.

Only one alloy has been prepared in each of the ternary chromium-boron systems. These had compositions selected so as to produce one volume percent of precipitate of titanium di-boride  $\text{TiB}_2$  or columbium di-boride  $\text{CbB}_2$ . All the alloy compositions used are listed in Table 6.

#### 4.2. Alloys containing Carbon

The alloys containing carbon were cast as 60 gram argon arc cast buttons and were examined as-cast and after heat treatment for 19 hours at  $2,250^\circ\text{F}$  ( $1,230^\circ\text{C}$ ). The structure and hardness results are summarised in Table 7 which also contains the results from samples of the extruded alloy containing tantalum and carbon. The carbides were identified by X-ray diffraction analysis after they had been extracted electrolytically; their compositions were obtained by comparing their lattice parameters with values quoted by Goldschmidt<sup>(10)</sup> for the variation in lattice parameters with degree of stoichiometry. All the refractory metal carbides had lattice parameters smaller than those corresponding to the fully stoichiometric composition; this is not unusual in precipitated carbide.

The compositions of the chromium matrix were estimated by comparing lattice parameters of the alloy and that of unalloyed chromium. The value for unalloyed chromium was measured from a sample of the chromium flake used in this research which was annealed for fifteen hours at the same temperature in hydrogen; this gave a lattice parameter of  $2.8845\text{\AA}$  which compares satisfactorily with the accepted value of  $2.8839\text{\AA}$ . (11) Auld and Ryan (12) have determined the variation in lattice parameter of chromium-tantalum solid solutions and they have shown that the mean increase in the lattice parameter from 0-2.4 atomic percent tantalum is  $0.0048\text{\AA}$  per atomic percent tantalum. No data are available for lattice parameters in chromium-titanium or chromium-columbium alloys; for this reason it has been assumed that the lattice parameter of chromium increases linearly with composition from  $2.8845\text{\AA}$  in pure chromium to  $3.284\text{\AA}$  in pure titanium and to  $3.306\text{\AA}$  in pure columbium. These assumptions give an increase in lattice parameter of  $0.0040\text{\AA}$  and  $0.0042\text{\AA}$  per atomic percent of titanium and columbium respectively. The accuracy of the lattice parameter measurements are estimated to be  $\pm 0.0001\text{\AA}$ ; thus the compositions are considered to be accurate to  $\pm 0.05\%$ . The data obtained from these measurements are summarised in Table 7 and micrographs of the cast alloys are reproduced in Figures 8a and 8b.

From these results the following conclusions have been drawn:-

- (i) All alloys in which the ratio of refractory metal to carbon was unity or less contained  $\text{Cr}_{23}\text{C}_6$  in the as-cast condition. These alloys also contained insoluble titanium or columbium carbides as can be deduced from the lattice parameters and the estimated matrix compositions.
- (ii) When the alloys with refractory metal to carbon ratio of 1 were heat treated at  $2,250^\circ\text{F}$  ( $1,230^\circ\text{C}$ ) the chromium carbide,  $\text{Cr}_{23}\text{C}_6$  which precipitated during casting, redissolved and further precipitation of the refractory metal carbide took place. This was not stoichiometric and varied from 41 atomic percent carbon in columbium carbide to 48 atomic percent carbon in the titanium carbide. This precipitation of the refractory metal carbide caused the significant decrease in lattice parameter and corresponding increase in hardness.
- (iii) In alloys containing refractory metal to carbon ratios greater than one, no chromium carbide was found in the as-cast state.
- (iv) On heat treatment at  $2,250^\circ\text{F}$  ( $1,230^\circ\text{C}$ ) precipitation appeared to be more affected in the titanium-containing alloys than in the columbium-containing alloys. Lattice parameters corresponding to an estimated titanium content of 0.12-0.17 percent titanium were obtained, whereas the corresponding figures in the columbium alloys varied from 0.17 atomic percent to 0.25 atomic percent columbium. The corresponding figure for the one alloy containing tantalum was 0.13 atomic percent tantalum.

It is noticeable in Table 7 that the alloys containing an excess of the refractory metal retained a higher metal solute content in the chromium lattice after precipitation and this may be detrimental to the retention of a low ductile/brittle transition temperature. However, these differences in solute contents are barely, if at all, outside the estimated experimental error and other factors suggest it may be advisable to retain an excess of refractory metal over the theoretical ratio. In particular, it is desirable to avoid the precipitation of the chromium carbide,  $\text{Cr}_{23}\text{C}_6$ , which would have a more deleterious effect on both ductility and toughness than slight excess of refractory metal in solid solution.

As both the systems containing carbon showed evidence of precipitation of a refractory metal carbide, it was decided to prepare larger casts of alloys from both of them. It was also intended to carry out a limited programme of bend test on strip prepared from the small 60 gram melt to estimate that the conclusions drawn above were correct. However, the grain structure of the as-cast buttons was not conducive to easy fabrication into sheet and no satisfactory sheet was produced.

#### 4.3. Alloys Containing Boron

Two alloys were made up containing respectively one volume percent of titanium di-boride,  $\text{TiB}_2$ , and one volume percent of columbium di-boride,  $\text{CbB}_2$ .

The experiments carried out on these alloys are summarised in Table 8. Heat treatments were carried out at three temperatures,  $2,192^\circ\text{F}$  ( $1,250^\circ\text{C}$ ),  $2,552^\circ\text{F}$  ( $1,400^\circ\text{C}$ ) and  $2,876^\circ\text{F}$  ( $1,580^\circ\text{C}$ ). In all cases, the diffraction data obtained from the electrolytically extracted precipitates indicated that the only precipitate present was  $\text{Cr}_4\text{B}$  and good agreement was obtained with the X-ray crystallographic data determined by Bertaat and Blun.<sup>(13)</sup> Micrographs of these alloys are shown in Figures 9 and 10 from which it can be seen that continuous bands of the boride were obtained at grain boundaries when alloys were slowly cooled after heat treatment. Such a distribution is not conducive to high ductility.

The micro-structure obtained in Figure 9b suggests that the solidus temperature may have been reached or exceeded; indeed this alloy heat treated at this temperature was the only one which contained any evidence of a phase other than the chromium boride,  $\text{Cr}_4\text{B}$ . The X-ray diffraction pattern of an extract from this alloy included an NaCl type cubic pattern with lattice parameter equal to  $4.44\text{\AA}$  and spectrographic analysis of the extract showed it to be rich in columbium and boron. The evidence for the existence of a cubic columbium boride is uncertain; some workers have reported such a structure<sup>(15)</sup> but others claim that this is a ternary compound containing nitrogen, carbon or oxygen. However, if this cubic columbium boride does form, there was no evidence that it precipitated from the chromium lattice on cooling and there would appear to be no advantage in

continuing the examination of boron-containing alloys. It would be necessary to determine the range of boron, titanium and columbium content over which the precipitation of  $\text{Cr}_4\text{B}$  could be avoided and at this stage of the research, it was not possible to include this more extensive programme. Therefore no further work has been carried out on alloys containing boron.

#### 4.4. Development of Specific Alloys Containing Carbon and Refractory Metals

##### 4.4.1. Manufacture

Three chromium-carbon alloy compositions were selected containing-wt % 1.1% columbium, 2.3% tantalum and 0.8% titanium respectively. A 2.75 kilogramme ingot in each composition given in Table 10 was prepared by consumable arc melting. These were machined 2 $\frac{1}{8}$ " (5.4 cm) diameter and extruded to 0.5" (1.3 cm) diameter after annealing for 90 minutes at 2,460 $^{\circ}\text{F}$  (1,360 $^{\circ}\text{C}$ ) in hydrogen.

The compositions of ingots, CA 122 and CA 124, were similar to those of the small argon arc melts, AA454 and AA462 i.e. they contained excess refractory metal. The tantalum and carbon levels of CA 123 were increased from those of CA 100 so that all three alloys had similar carbon levels and precipitate densities (Table 10).

Lengths of the extruded bar were machined to remove any irregularities and then were sheathed in a mild steel cylinder, 1" (2.5 cm) diameter to which an end cap was welded. After heating to 2,120 $^{\circ}\text{F}$  (1,160 $^{\circ}\text{C}$ ) they were then rolled to  $\frac{1}{2}$ " (1.3 cm) diameter overall; after removing the sheath, the rolled chromium bar was  $\sim \frac{1}{4}$ " (0.64 cm) diameter. Material in this condition is referred to later as the rod rolled or warm worked condition.

Attempts were made to prepare strip from the  $\frac{1}{4}$ " (0.64 cm) diameter chromium alloy rod either unsheathed or in their original sheath but in neither condition was it possible to produce sound sheet without severe cracking. In view of the limited amount of material available it was decided to abandon further attempts to produce sheet material. Therefore, the transition temperatures for these alloys have been obtained using round tensile specimens prepared from the rod rolled material. X-ray examination of samples from the tantalum alloy showed that the rod rolled material had a partial recovered structure. The samples were highly textured with most of the grains oriented with  $\langle 110 \rangle$  directions within  $\pm 5^{\circ}$  of the extrusion or rolling direction.

##### 4.4.2. Effect of Heat Treatment on Structure and Properties

A series of heat treatments have been undertaken to determine whether it is possible to improve the strength of the as-rolled material by

redissolving the carbides and precipitating them on a finer scale at a temperature above the intended service temperature. The effect of the heat treatment was studied by hardness measurements and optical metallography.

Rolled samples of the three alloys were heat treated individually in purified hydrogen for  $2\frac{1}{2}$  hours at  $3,000^{\circ}\text{F}$  ( $1,650^{\circ}\text{C}$ ); they were then quenched into oil. Each sample was cut into several smaller pieces and these were aged at  $2190^{\circ}\text{F}$  ( $1,200^{\circ}\text{C}$ ) together with similar samples from as-rolled material which had not been subjected to the solution treatment. Specimens were removed after ageing for 1, 4, 8 and 16 hours; the results of hardness tests are presented in Table 11.

Metallographic examination showed that this solution treatment at  $3,000^{\circ}\text{F}$  ( $1,650^{\circ}\text{C}$ ) caused complete recrystallisation to an equiaxed structure of large grain size. Some grain boundary  $\text{Cr}_{23}\text{C}_6$  was present in the columbium alloy but was absent from the other two. In the alloy containing columbium, ageing the rolled material caused the hardness to fall to a constant value of just below 200 Hv10. Whilst the solution treatment increased the hardness, the effect was transient and after ageing for four hours, a constant hardness of 200 Hv10 was maintained. The alloy with tantalum responded in a similar way and the hardness of 200-210 Hv10 was obtained irrespective of whether the alloy had been solution-treated or not. The hardness of the alloy with titanium however, was appreciably lower (155-165 Hv10) after solution treatment than after ageing the as-rolled material (180-185 Hv10). In this alloy, however there was some scatter in hardness and the alloy may continue to soften on ageing for longer periods.

Thus the general conclusion from these heat treatments is that the solution treatment is not likely to improve the strength of any of the alloys; it may in fact be disadvantageous in that it increases the grain size considerably and this would be expected to reduce the toughness and ductility.

#### 4.4.3. Mechanical Tests

Mechanical tests have been carried out on all three alloys in the conditions extruded and rolled at  $2,120^{\circ}\text{F}$  ( $1,160^{\circ}\text{C}$ ); this will be referred to as the warm worked condition.

Tensile tests at low temperatures have also been carried out on the alloys containing tantalum and columbium after a heat treatment of four hours at  $2,370^{\circ}\text{F}$  ( $1,300^{\circ}\text{C}$ ) which caused partial recrystallisation. This treatment was intended to simulate the effect of excursions to high temperatures on the ductile/brittle transition temperature of these alloys.



Two groups of tests were made, firstly tensile test at temperatures from 122°F (50°C) to 572°F (300°C) to determine the ductile/brittle transition temperature; secondly, tensile and creep tests at 1,900°F (1,038°C) and 2,100°F (1,149°C).

The low temperature tensile tests (Table 12) showed that the ductile/brittle transition temperature was between 122°F (50°C) and 212°F (100°C) for the alloys containing columbium and tantalum; however, it was above 212°F (100°C) and below 414°F (212°C) in the titanium-containing alloy. The annealing treatment at 2,370°F (1,300°C) reduced the temperature of the ductile/brittle transformation in both the alloys containing columbium and tantalum to below 122°F (50°C), at which elongations of 10% and 6% were obtained for these two alloys respectively. In general, the alloy containing columbium had the highest ductility and that containing titanium the lowest.

In tensile tests at elevated temperatures, 0.2% yield stresses of 18.3 tonf/in<sup>2</sup> (282 MN/m<sup>2</sup>) and 12.8 tonf/in<sup>2</sup> (198 MN/m<sup>2</sup>) were achieved in the alloy with tantalum at 1,900°F (1,038°C) and 2,100°F (1,149°C) respectively. The corresponding figures for the columbium-bearing alloy were 16.9 tonf/in<sup>2</sup> (261 MN/m<sup>2</sup>) and 10.3 tonf/in<sup>2</sup> (159 MN/m<sup>2</sup>) and for the titanium-bearing alloy 13.8 tonf/in<sup>2</sup> (213 MN/m<sup>2</sup>) and 10.2 tonf/in<sup>2</sup> (157 MN/m<sup>2</sup>).

The stress-rupture data (Table 13) also showed the tantalum containing alloy to have highest resistance to deformation at high temperatures; the alloys containing columbium and titanium were less creep resistant in that order.

The differences between the three alloys are shown most clearly in the Larson-Miller plot in Figure 4. This figure also shows the comparison between the alloys examined in this research and the published data particularly that by the Australian workers who also show the superiority of the tantalum-bearing chromium-alloys. From the data in Figure 4, Table 14 had been derived; this shows the stresses estimated to cause failure in 10 and 100 hours at both 1,900°F (1,038°C) and 2100°F (1149°C).

#### 4.4.4. Conclusions

The detailed study of the chromium alloys containing carbon and refractory metals has led to four conclusions.

- (i) Better high temperature properties are obtained from alloys containing a refractory metal like tantalum from the third long period of the periodic table than one like titanium or columbium from the first and second long periods.
- (ii) On the limited evidence obtained, elements from group V (columbium) provide better creep resistance than those from group IV (titanium).

Unfortunately, no data were obtained from alloys containing zirconium which could be compared directly with the data from the columbium-bearing alloy.

- (iii) The warm worked structure gave very good stability at the temperatures considered. Partial recrystallisation of this structure in two of the alloys decreased the temperature of the ductile/brittle transition to below 122°F (50°C); this is an extremely important finding and should be investigated in more detail.
- (iv) The alloy with columbium was more ductile at low temperatures than the one with tantalum. Despite the lower creep resistance of the columbium bearing alloy, its greater ductility may show it to be superior to the one with tantalum. This factor and the evidence from Ryan's work that combined additions of refractory elements in alloys containing carbon increased creep resistance still further would justify further examination of these alloys.

## 5. GENERAL DISCUSSION AND CONCLUSIONS

The first objective of making high strength chromium-base alloys by precipitation of a binary chromium-free intermetallic compound of high enthalpy was not achieved. In all cases where a precipitate was obtained, it was either a binary phase containing chromium or a ternary phase. More important, in no case did precipitation deplete the chromium matrix of solute element and therefore these alloys would have been expected to have a relatively high ductile/brittle transition temperature.

The second phase of the research was much more successful and chromium-carbon alloys containing tantalum or columbium were produced with good creep resistance combined with ductility at 216°F (102°C) in the warm-worked conditions. Partial recrystallisation of this structure decreased the ductile/brittle transition temperature still further and provided alloys with ductility at 122°F (50°C). Whilst the columbium-bearing alloys did not have the best creep resistance, they were more ductile. Further work on combined additions of carbide forming metals in chromium carbon alloys is strongly recommended.

Substitution of boron for carbon caused precipitation of chromium boride and not a refractory metal boride. The effect of small additions of boron to carbon bearing alloys has not been examined and this may well be worthwhile in conjunction with the further work on combined additions of carbide forming elements.

## 6. ACKNOWLEDGEMENTS

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TABLE 1  
Micro structure and hardness of the 1 and 5

Alloy No.	Nominal Composition Wt%	As Cast	Water Quenched from 2732°F (1500°C)	Water Quenched from 3002°F (1650°C)
AA384	0.16Si 0.46 Ti 1 vol% Ti <sub>5</sub> Si <sub>3</sub> Hardness H <sub>V</sub> 10	Few globules of pink phase. 143		155
AA383	2.32 Ti 0.82 Si 5 vol% Ti <sub>5</sub> Si <sub>3</sub> Hardness H <sub>V</sub> 10	Few globules of pink phase 260		
AA391	2.32Ti 1.33Si (5 vol% Ti <sub>5</sub> Si <sub>3</sub> + excess Si Hardness H <sub>V</sub> 10	Few globules of pink phase Similar to AA383 275		
AA387	0.10Ti 0.23Be 1 vol% Ti Be <sub>12</sub> Hardness H <sub>V</sub> 10	Some intragranular and intergranular globules of a compound. 200		Similar to as-cast structure. 210
AA388	0.50Ti 1.14Be 5 vol% TiBe <sub>12</sub> Hardness H <sub>V</sub> 10	Some globules and grain boundary particles. 460		
AA382	0.76 Zr 0.12 Si 1 vol% Zr <sub>2</sub> Si Hardness H <sub>V</sub> 10	Particles and grain boundary network of compound. 152		Similar to the as cast structure 155
AA381	3.80 Zr 0.58 Si 5 vol% Zr <sub>2</sub> Si Hardness H <sub>V</sub> 10	Continuous grain boundary network of compound. (Fig.6) 175		
AA385	0.24Zr 0.20Be 1 vol% Zr <sub>2</sub> Be <sub>17</sub> Hardness H <sub>V</sub> 10	Some globules and some elongated particles at grain boundaries. 180	Similar to as cast structure. 187	Similar to as cast structure. 210
AA386	1.20Zr 1.01Be 5 vol% Zr <sub>2</sub> Be <sub>17</sub> Hardness H <sub>V</sub> 10	Large amount of intra-granular and grain boundary compound (Fig.7a) 382		

volume & alloys produced by various heat-treatments

15 hrs. at 2102°F (1150°C) Furnace Cooled	15 hrs. at 2372°F (1300°C) Furnace Cooled	15 hrs. at 2552°F (1400°C) Furnace Cooled	15 hrs. at 2732°F (1500°C) Furnace Cooled
	Similar to as cast structure. 138		
	Similar to as cast structure.		
		Similar to as cast structure 205	Similar to as cast structure. 197
Fine interdendritic precipitation with dendrites free from precipitate. 308	More clearly defined primary particles plus a large amount of fine precipitation. (Fig. 5) 390	Dense fine precipitation with some evidence of dendritic segregation. 510	Dense fine precipitation - no segregation. 463
	Similar to the as cast structure. 135		Similar to the as cast structure. 141
	Similar to the as cast structure. 160		
	Some fine precipitation (Fig. 7c) 160	Fine precipitation but not so fine at 1300°C. 148	
Fine fairly uniform precipitation. Primary particles had decomposed into two phases. (Fig. 7b) 273	Similar to the 1150°C heat treatment. 300	Fine precipitation. Primary particles decomposed into two phases. 426	Fine precipitation but not very dense. 412

TABLE 2

Summary of Findings on Chromium Intermetallic Alloy Systems  
for compositions calculated to give 1 and 5 volume percent  
of anticipated intermetallic compound

Alloy Additions	Zirconium		Titanium	
	Compounds	Remarks	Compounds	Remarks
Beryllium	$\text{Zr Cr}_2$ $\text{Zr Be}_2$ $\text{Zr (N, O, C)}$	Initial alloys primary phase in as cast condition. Zr level above solubility for Zr in Cr. Low Zr alloys (0.12 at% Zr) compounds as shown. Beryllium still in solid solution with ppts of $\text{ZrCr}_2$ and $\text{Be Cr}_2$ .	Probably: $\text{Be}_2\text{Cr}$	Since $\text{Be}_2\text{Cr}$ is precipitating instead of $\text{TiBe}_{12}$ , titanium is left in solid solution where it increases hardness and reduces low temperature ductility.
	Anticipated Compound $\text{Zr}_2\text{Be}_{17}$		Anticipated Compound $\text{Ti Be}_{12}$	
Silicon	$\text{Cr}_6\text{Zr}_2\text{Si}$ or $\text{Cr}_5\text{Zr}_4\text{Si}$	Not an effective precipitation hardening system. Hardnesses little changed by heat treatments.	No precipitated compounds. A few unidentified pink particles present.	Hardness related to solid solution hardening. No susceptibility to heat treatment.
	Anticipated Compound $\text{Zr}_2\text{Si}$		Anticipated Compound $\text{Ti}_5\text{Si}_3$	

TABLE 3

Hardness of Extruded Cr-Zr-Be Alloys

Alloy	Composition		As-Extruded Hardness $H_{V10}$	Hardness after ageing 15 hrs. 2282°F (1250°C) $H_{V10}$
No.	a/o Zr	a/o Be		
CA117	0.12	0.94	181	170
CA118	0.12	2.33	260	256

TABLE 4

Hardness and Texture of Alloys in Various Conditions.

Alloy No.	Composition At.%	As Extruded	Rod Rolled from 2102°F (1150°C)	Rod and Strip rolled from 2102°F (1150°C)	Rod rolled from 2102°F (1150°C) and strip rolled from 1382°F (750°C)	Rod rolled from 2102°F (1150°C) and strip rolled from 1382°F (750°C) + 15 hrs. at 2282°F (1250°C)
CA117	0.12 Zr 0.94 Be	181 H <sub>V</sub> 10  Textured with a <110> direction along the extrusion direction.	235 H <sub>V</sub> 10  Textured with a <110> direction along the rolling directions.	290 H <sub>V</sub> 10  Sharply textured with (112) <110> (001) <110> (111) <112> components. Partially recrystallized structure.	323 H <sub>V</sub> 10  Sharply textured with (112) <110> and (001) <110> (111) <112> components. Worked structure.	166 H <sub>V</sub> 10  Textured with (112) <110> and (001) <110> (111) <112> components. Fully recrystallized structure.
CA118	0.12 Zr 2.33 Be	260 H <sub>V</sub> 10	337 H <sub>V</sub> 10			



TABLE 5

Results of Bend Test on Alloy CA117

(0.12 at % Zr 0.94 at % Be) Annealed

15 hrs. at 1250°C

Strain Rate  $\sim 10^{-2}$ /min

Specimen No.	Surface Preparation	Temperature of Test	Maximum Fibre Stress at Yield tons/sq." (MNm <sup>-2</sup> )	Remarks
D3	Electropolished	(250°C) 482°F		Fractured during elastic region.
D1	Electropolished	(300°C) 572°F		Plastic deformation preceded fracture.
D4	Mechanically polished prior to electropolishing.	(300°C) 572°F	30 (462)	Plastic deformation preceded fracture. Larger amount of plastic deformation than occurred with Specimen No. D1. Cleavage fracture.
D2	Electropolished	(350°C) 482°F		Plastic deformation preceded fracture. Cleavage fracture.

TABLE 6

Nominal Composition of the Alloys

Cast No.	Composition Wt% (At%)			Atom Ratio $\frac{\text{Ti or Cb}}{\text{C or B}}$	Remarks
	Ti	Cb	C or B		
AA457	0.55 (0.59)		0.14C (0.59) C	1.0	Stoichiometric Ti/C to precipitate 1 vol% TiC.
AA458	0.55 (0.60)		0.14C (0.62) C	0.96	Excess carbon to ensure formation of TiC if $\text{Cr}_{23}\text{C}_6$ is present.
AA459	0.83 (0.89)		0.14C (0.59) C	1.50	Excess titanium to allow for any solid solution in the matrix in addition to the formation of 1 vol% TiC.
AA460		0.96 (0.54)	0.12C (0.54) C	1.0	Stoichiometric Cb/C to precipitate 1 vol% CbC.
AA461		0.96 (0.54)	0.13C (0.56) C	0.96	Excess carbon to ensure formation of CbC if $\text{Cr}_{23}\text{C}_6$ is present.
AA462		1.20 (0.67)	0.12C (0.54) C	1.25	Excess Columbium to allow for any solid solution in the matrix in addition to the formation of 1 vol% CbC.
AA467	0.43 (0.47)		0.19B (0.93) B	0.50	Stoichiometric $\text{TiB}_2$ to precipitate 1 vol%.
AA468		0.79 (0.44)	0.19B (0.88) B	0.50	Stoichiometric $\text{CbB}_2$ to precipitate 1 vol%.
CA 100	2.00Ta (0.58) Ta		0.08C (0.35) C	1.65	Excess tantalum in addition to 0.65 vol% TaC.

TABLE 7

## Structure of As Cast and Heat Treated Carbide Alloys

Cast No.	Composition (Nominal) Wt% (at%) Atomic Ratio		Heat Treatment	Hardness H <sub>10</sub> V	Matrix* Lattice Parameter and Composition	Residue	Structure
	Ti	C					
AA457	0.55 (0.59)	0.14 (0.59)	As cast	162	2.8858Å <sup>0</sup> 0.32at%Ti	Cr <sub>23</sub> C <sub>6</sub> * a=10.665Å <sup>0</sup> <sub>8</sub>	Grain boundary Cr <sub>23</sub> C <sub>6</sub> and Ti C precipitates. A few coarse intragranular Ti C particles together with some finer precipitates.
		$\frac{\text{Ti}}{\text{C}} = 1$	15 hrs. 2246°F (1230°C)	182	2.8850Å <sup>0</sup> 0.12at%Ti	Cr+Ti C* a <sub>Ti C</sub> =4.327Å <sup>0</sup> ~Ti48at%C	Small amount of grain boundary Ti C. A few coarse intragranular Ti C particles together with a much finer and denser precipitate of Ti C.
AA458	0.55 (0.60)	0.14 (0.62)	As cast	160			Grain boundary Cr <sub>23</sub> C <sub>6</sub> and Ti C precipitates. A few coarse intragranular Ti C particles together with some finer precipitates.
		$\frac{\text{Ti}}{\text{C}} = 0.96$	15 hrs. 2246°F (1230°C)	187	2.8851Å <sup>0</sup> 0.15at%Ti	Ti C + Titanium Oxide a <sub>Ti C</sub> =4.325Å <sup>0</sup> ~Ti48at%C	Small amount of grain boundary Ti C. A few coarse intragranular Ti C particles together with a Ti C precipitate which is much finer and denser than that present in the as cast condition.
AA459	0.83 (0.89)	0.14 (0.59)	As cast	186	2.8856Å <sup>0</sup> 0.28at%Ti		Small amount of grain boundary Cr <sub>23</sub> C <sub>6</sub> which is much less than that present in alloys AA457 and AA458. There is also some grain boundary Ti C and a few coarse intragranular Ti C particles together with a finer intragranular precipitate.
		$\frac{\text{Ti}}{\text{C}} = 1.50$	15 hrs. 2246°F (1230°C)	187	2.8852Å <sup>0</sup> 0.17 at%Ti O	Ti C + Titanium Oxide a <sub>Ti C</sub> =4.325Å <sup>0</sup> ~Ti48at%C	Small amount of grain boundary Ti C with some coarse intragranular Ti C particles. There is also a fine dense intragranular Ti C precipitate.

\* Pure chromium has lattice parameter 2.8845Å<sup>0</sup>

TABLE 7 (continued)

Cast No.	Composition (Nominal) Wt% (at%)		Heat Treatment	Matrix* Lattice Parameter and Composition	Residue	Structure
	Cb	C				
AA460	0.96 (0.54)	0.12 (0.54)	As cast	2.8860 $\text{\AA}$ 0.35at%Cb		Grain boundary $\text{Cr}_{23}\text{C}_6$ and Cb C. A few coarse CbC intragranular particles with a finer CbC precipitate.
		$\frac{\text{Cb}}{\text{C}} = 1.00$	19 hrs. 2246 $^{\circ}\text{F}$ (1230 $^{\circ}\text{C}$ )	2.8855 $\text{\AA}$ 0.24at%Cb	Cr + CbC* $a_{\text{CbC}} = 4.433\text{\AA}$ $\sim 41\text{at}\% \text{C}$	Some grain boundary CbC and a few coarse CbC intragranular particles together with a fairly uniform dense intragranular CbC precipitate.
AA461	0.96 (0.54)	0.13 (0.56)	As cast			Grain boundary $\text{Cr}_{23}\text{C}_6$ and Cb C. A few coarse Cb C intragranular particles together with a finer intragranular Cb C precipitate.
		$\frac{\text{Cb}}{\text{C}} = 0.96$	19 hrs. 2246 $^{\circ}\text{F}$ (1230 $^{\circ}\text{C}$ )	2.8852 $\text{\AA}$ 0.17at%Cb	Cb C $a = 4.443\text{\AA}$ $\sim 43\text{at}\% \text{C}$	Some Cb C at the grain boundaries. A few coarse intragranular Cb C particles together with a fairly uniform dense intragranular Cb C precipitate.
AA462	1.20 (0.67)	0.12 (0.54)	As cast	2.8860 $\text{\AA}$ 0.35at%Cb		No grain boundary $\text{Cr}_{23}\text{C}_6$ . Some Cb C at the grain boundaries. There are a few coarse intragranular Cb C particles together with a finer intragranular Cb C precipitate.
		$\frac{\text{Cb}}{\text{C}} = 1.25$	19 hrs. 2246 $^{\circ}\text{F}$ (1230 $^{\circ}\text{C}$ )	2.8856 $\text{\AA}$ 0.25at%Cb	Cr + Cb C* $a_{\text{CbC}} = 4.435\text{\AA}$ $\sim 41\text{at}\% \text{C}$	Some Cb C at the grain boundaries. A few coarse intragranular Cb C particles together with a fairly uniform dense intragranular Cb C precipitate.
CA100	2.0CTa (0.58)	0.08C (0.35)	As extruded		Ta C $a = 4.437\text{\AA}$ 46.8at%C	Fine precipitate particles, some alignment parallel to the extrusion direction.
		$\frac{\text{Ta}}{\text{C}} = 1.65$	15 hrs. 2282 $^{\circ}\text{F}$ (1250 $^{\circ}\text{C}$ )	2.8851 $\text{\AA}$ 0.13at%Ta		Similar to the extruded condition.

\* Pure chromium has lattice parameter 2.8845 $\text{\AA}$

TABLE 8

Structures of CrTiB and CrCb B Alloys After Various Heat Treatments

Alloys	As Cast	Heat Treatment - furnace cooled after:-				Comment
		24 hrs. 2282°F (1250°C)	24 hrs. 2552°F (1400°C)	15 hrs. 2822°F (1550°C)	15 hrs. 2876°F (1580°C)	
CrTiB 1 vol %TiB <sub>2</sub> AA 467	Grain boundary network and coarse dispersed phase of Cr <sub>4</sub> B.	Same as As cast	Ppt. extracted Cr <sub>4</sub> B	Coarse grain boundary and intergranular phase of Cr <sub>4</sub> B 135 H <sub>v</sub> 10.	Ppt. extracted Cr <sub>4</sub> B but grain boundary network broken up.	Although Cr <sub>4</sub> B appears to dissolve and reprecipitate at 1580°C no titanium borides have formed.
CrCbB 1 vol %CbB <sub>2</sub> AA 468	Grain boundary network and coarse dispersed phase of Cr <sub>4</sub> B.	Same as As cast	Ppt. extracted Cr <sub>4</sub> B	Coarse grain boundary and intergranular Cr <sub>4</sub> B 178 H <sub>v</sub> 10.	Ppt. cubic of NaCl type structure some Cr <sub>4</sub> B. Ppt. may be metastable CbB Wide grain boundary phase. Coarse dispersed intergranular phase. Signs of structure within the network and intergranular phase.	Below 2876°F (1580°C) second phase is Cr <sub>4</sub> B but at 1580°C a reaction is taking place but grain boundary network is still coarse and there is no fine precipitation.

TABLE 9

Analysis of the diffraction data from the material  
extracted from the as cast CrTiB alloy AA467

AA467 as cast			Cr <sub>4</sub> B*			Ti B <sub>2</sub>		
Id No.	Int	d	d	hkl	$\frac{I}{I_0}$	d	hkl	$\frac{I}{I_1}$
1	w	3.506	3.579	111	6			
2	w	3.225				3.22	001	20
3	w	2.936	2.949	311	5			
4	m	2.644				2.62	100	60
5	w	2.554						
6	ms	2.300	2.300	511	36			
7	m	2.178						
8	ms	2.113	2.108	131	72			
9	s	2.043	2.044	(202) (620)	97	2.033	101	100
10	w	1.954	1.953	331	20			
11	w	1.861	1.845	800	2			
12	m	1.825	1.826	711	30			
13	m	1.648	1.649	(422) (440)	56			
14	w	1.616				1.613	002	13
						1.514	110	19
15	w	1.444						
16	w	1.382				1.374	102	15
						1.370	111	10
17	mw	1.303	1.303	(822) (840)	38	1.311	200	7
18	w	1.281						
19	w	1.260	1.260	(513) (551)	47			
20	m	1.226	1.226	(1200) (133)	69			
21	m	1.213	1.212	(642) (1002)	100	1.215	201	14
22	m	1.162	1.162	(713) (751)	49			

Intensities s = strong

m = medium

w = weak

a = 14.71

\* Diffraction data for Cr<sub>4</sub>B orthorhombic Fddd b = 7.38

c = 4.26

Intensities calculated as multiplicity x (structure factor)<sup>2</sup>

TABLE 10

Extruded Alloys

Cast No.	Composition	As extruded hardness $H_{10V}$
CA 122	Cr 1.20wt%Cb 0.12 wt%C	199
CA 123	Cr 2.33 wt%Ta 0.12 wt%C	224
CA 124	Cr 0.83 wt%Ti 1.14 wt%C	195

TABLE 11

Hardness Values on Samples Aged at 2190°F (1200°C)

$H_{10V}$

Alloy No.	Nominal Composition	Starting Condition	Time at 2190°F (1200°C) hrs.				
			0	1	4	8	16
CA122	1.20Cb 0.12C	o.q.	228	231	201	203	201
		r.r.	212	204	197	196	199
CA123	2.33Ta 0.12C	o.q.	275	230	210	199	209
		r.r.	228	225	213	211	207
CA124	0.83Ti 0.14C	o.q.	182	182	160	166	155
		r.r.	217	200	165	185	182

o.q. Rod rolled and oil quenched after 2½ hours  
at 3,002°F. (1650°C)

r.r. Rod rolled.

TABLE 12

Tensile Properties of Alloys

Alloy wt%	Condition	Test Temperature		U.T.S.		0.5 YS	
		F°	C°	tonf/in <sup>2</sup>	MN/m <sup>2</sup>	tonf/in <sup>2</sup>	MN/m <sup>2</sup>
CA 122 1.20Cb 0.12C	As rolled 4 hrs 2372°F 1300°C	122	50	28.2	435	-	-
		122	50	30.9	469	17.1	264
	As rolled 4 hrs 2372°F 1300°C	216	102	38.2	590	30.1	464
		212	100	31.7	490	19.9	308
	As rolled	397	203	35.0	540	29.7	458
	As rolled	1900	1038	17.5	270	16.9 <sup>+</sup>	261
	As rolled	2100	1149	11.8	182	10.3 <sup>+</sup>	159
	As rolled 4 hrs 2372°F 1300°C	122	50	23.7	366	-	-
		122	50	35.9	555	23.6	364
	As rolled	216	102	41.2	635	32.5	502
CA 123 2.33Ta 0.12C	As rolled	401	205	37.0	571	31.7	489
	As rolled	1900	1038	18.9	292	18.3 <sup>+</sup>	282
	As rolled	2100	1149	13.7	212	12.8 <sup>+</sup>	198
	As rolled 4 hrs 2372°F 1300°C	122	50	35.3	545	32.4	500
		212	100	38.0	586	32.3	499
	As rolled	414	212	33.2	512	28.7	443
	As rolled	572	300	31.6	487	28.3	436
	As rolled	1900	1038	14.5	224	13.8 <sup>+</sup>	213
	As rolled	2100	1149	10.8	167	10.2 <sup>+</sup>	157
	As rolled	1900	1038	14.5	224	13.8 <sup>+</sup>	213
CA 124 0.83Ti 0.14C	As rolled	2100	1149	10.8	167	10.2 <sup>+</sup>	157

+ These values are 0.2 YS



CA 122, 123 and 124

Elongation %	R.A. %	Remarks
0	0	Fractured close to the shoulder. Probably nucleated by a defect at the shoulder.
10	10	Double fracture at the centre of the gauge length.
25	55	Double cup and cone fracture at the centre of the gauge length.
24	43	Double fracture at the centre of the gauge length.
25	76	Cup and cone fracture at the centre of the gauge length.
21	73	Cup and cone fracture.
26	80	Cup and cone fracture.
0	0	Fractured close to the shoulder. Probably nucleated by a defect at the shoulder.
6	4	Double fracture towards the centre of the gauge length.
11	9	Double cup and cone fracture towards the end of the gauge length. The largest RA occurred at the centre of the gauge length and not at the fracture.
26	71	Cup and cone fracture at the centre of the gauge length.
15	78	Cup and cone fracture.
24	77	Cup and cone fracture
1	0	Double cup and cone fracture towards the centre of the gauge length.
5	2	Double cup and cone fracture towards the centre of the gauge length.
25	55	Double cup and cone fracture towards the centre of the gauge length.
26	75	Cup and cone fracture.
21	83	Cup and cone fracture.
27	90	Cup and cone fracture.

TABLE 13

Stress Rupture Behaviour at 1900°F (1038°C) and 2,100°F (1149°C)  
in the as rod rolled condition

Alloy	Temp.	Stress tonf/in <sup>2</sup> MN/m <sup>2</sup>		Life Hrs.	R.A. %	Elongation %
CA 122 Cr 1.20 Cb 0.12 C	1900°F 1038°C	9.0	139	8.5	76	29
		8.8	136	46.0	72	29
		7.5*	116	54.0	35	29
		7.0	108	91.0	65	34
	2100°F 1149°C	5.7	88	10.8	80	39
		4.4	68	90.0	80	48
CA 123 Cr 2.33 Ta 0.12 C	1900°F	9.5	147	28.2	77	30
	1038°C	8.0	124	122.3	67	30
	2100°F 1149°C	6.5	100	18.2	80	43
CA 124 Cr 0.83 Ti 0.14 C	1900°F	9.0	139	3.7	85	31
	1038°C	5.8	90	251.0	17	30-35
	2100°F 1149°C	4.0	62	41.6	80	45

\* Test carried out under vacuum and not argon

TABLE 14

Stresses Estimated to give Rupture Lives  
of 10 and 100 hrs. at 1900°F (1038°C)  
and 2100°F (1149°C)

Alloy	Temp.	10 hours		100 hours	
		tonf/in <sup>2</sup>	MN/m <sup>2</sup>	tonf/in <sup>2</sup>	MN/m <sup>2</sup>
CA 122 Cr 1.20Cb 0.12C	1900°F 1038°C	9.5	147	7.1	110
	2100°F 1149°C	5.8	90	4.2	65
CA 123 Cr 2.33Ta 0.12C	1900°F 1038°C	11.0	170	8.2	127
	2100°F 1149°C	6.8	105	5.2	80
CA 124 Cr 0.83Ti 0.14C	1900°F 1038°C	8.4	130	6.2	96
	2100°F 1149°C	4.9	76	3.6	56

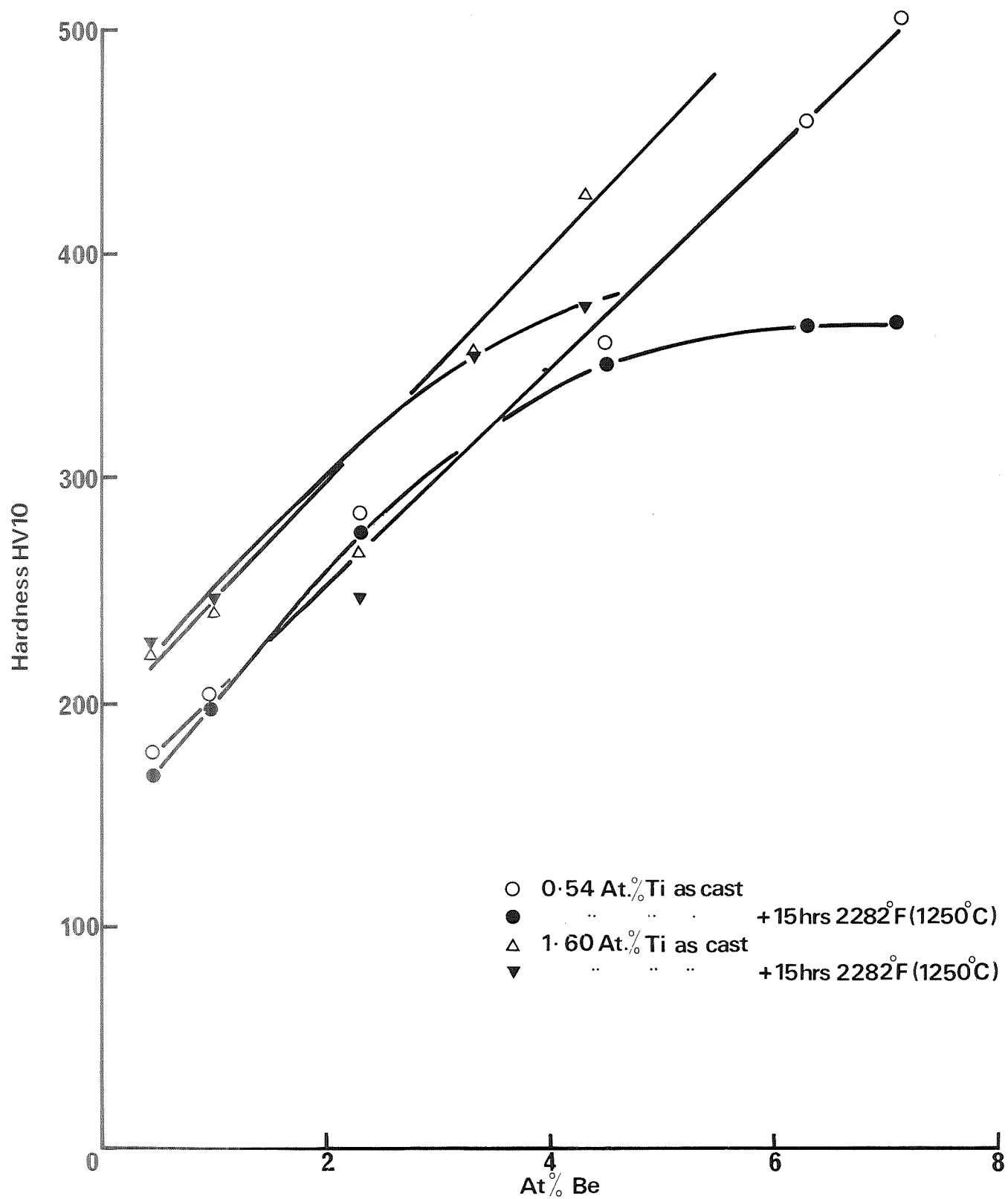


Figure 1. Effect of Beryllium on the hardness of Cr - Ti alloys.

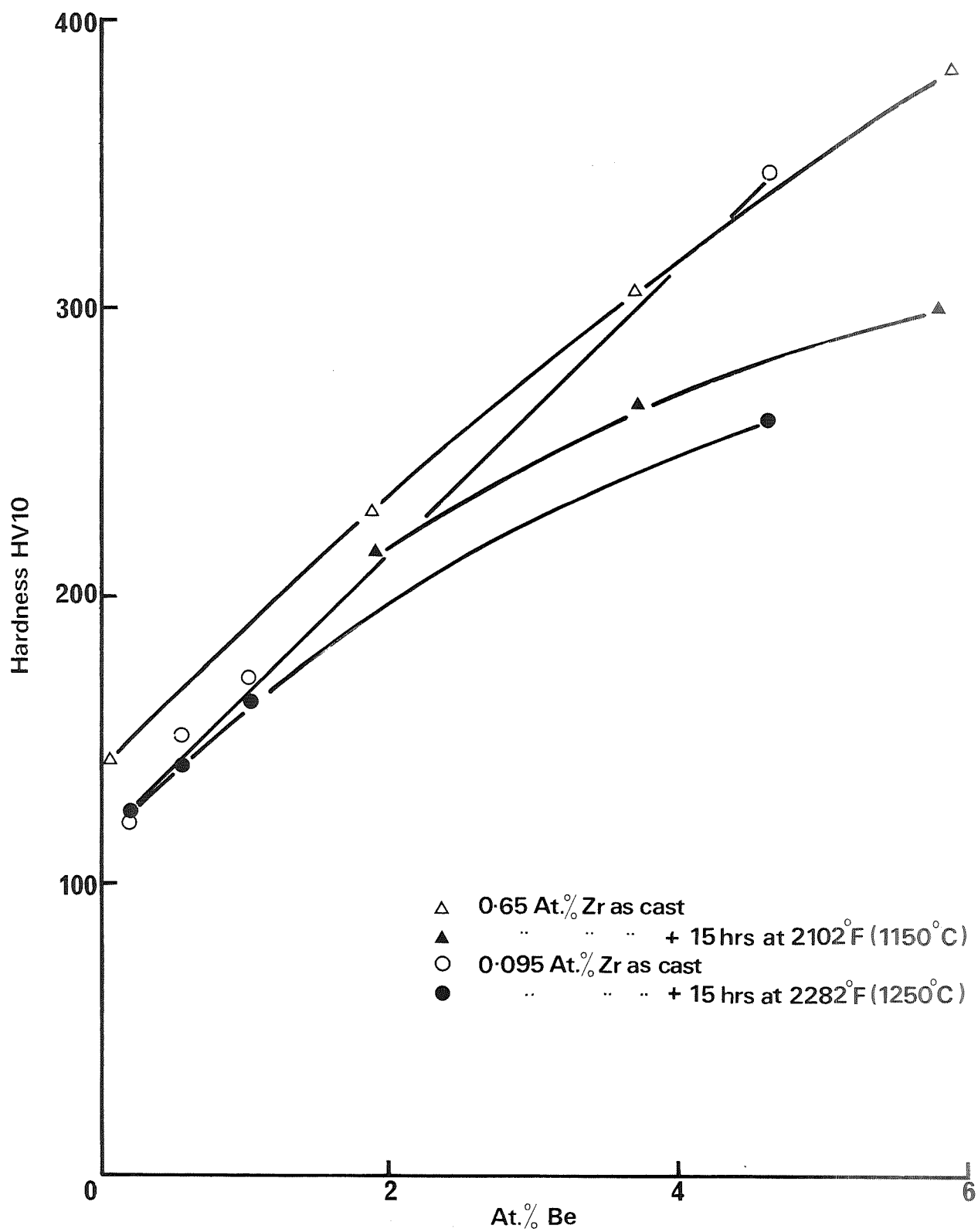


Figure 2.

Effect of Beryllium on the hardness of Cr - Zr Alloys.

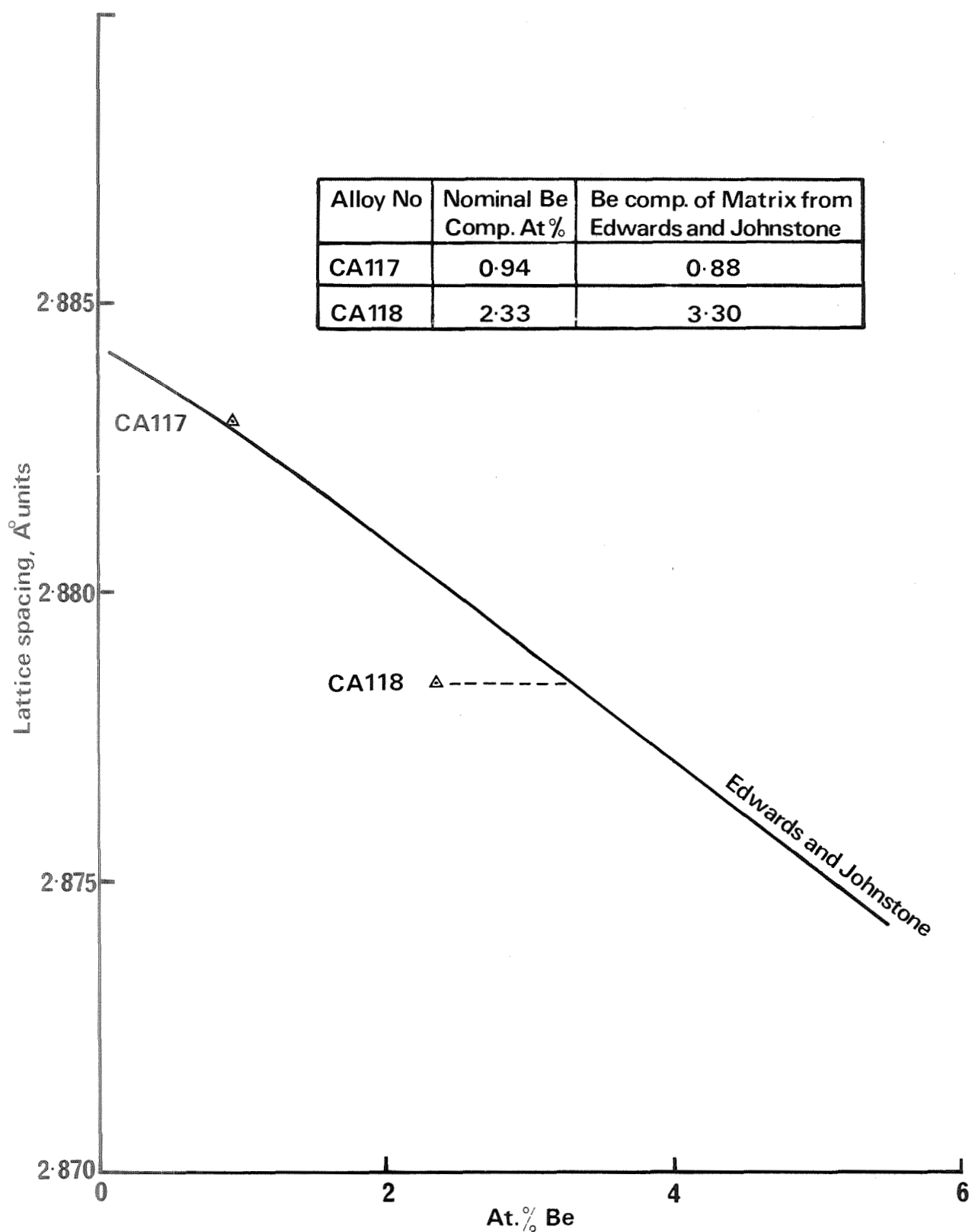
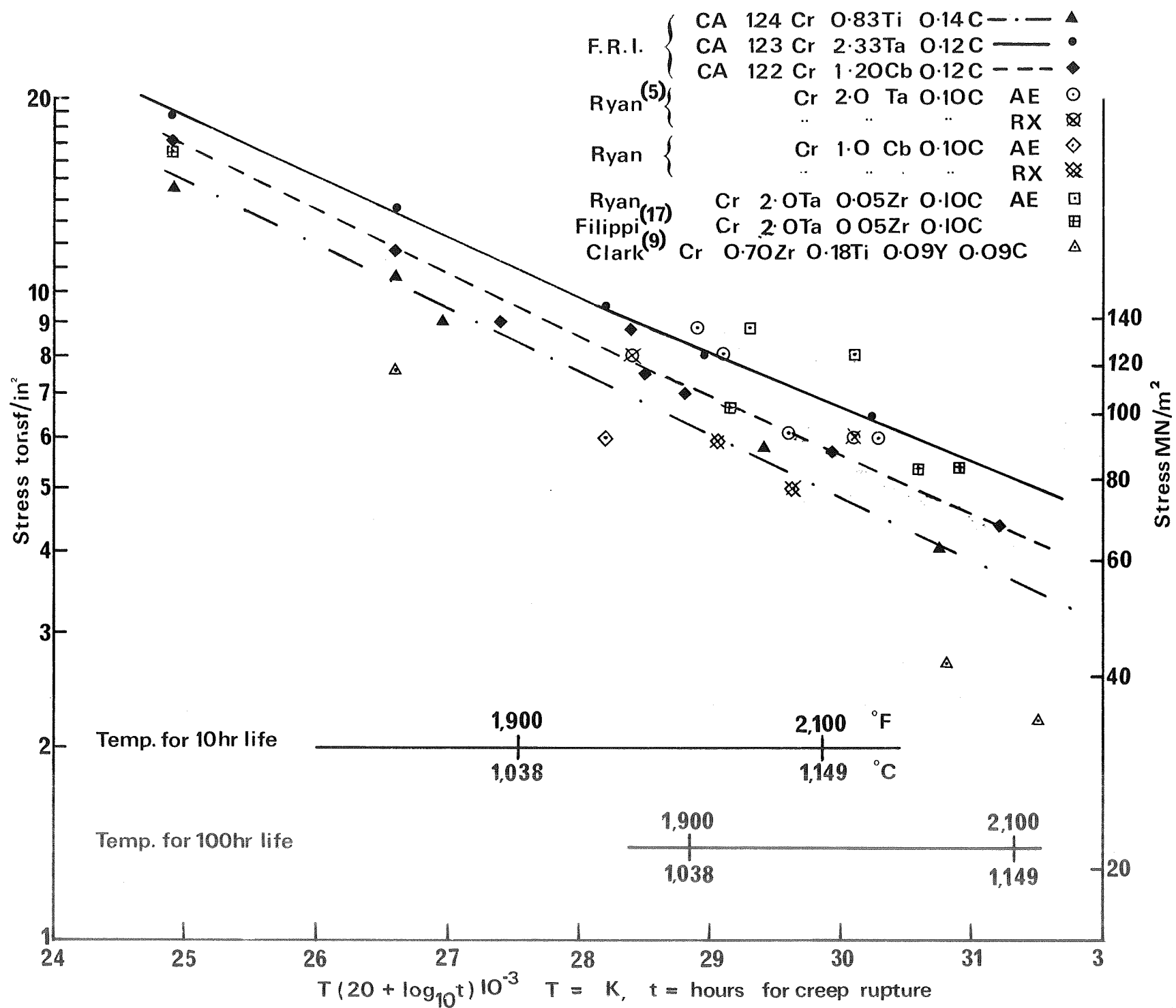


Figure 3. The lattice spacings of alloy CA117 (0.12Zr 0.94Be) and CA118 (0.12Zr 2.33Be) heat treated 15hrs at 2282°F furnace cooled compared with results obtained by Edwards and Johnstone.

Figure 4.

Larson - Miller time - to - rupture plot.



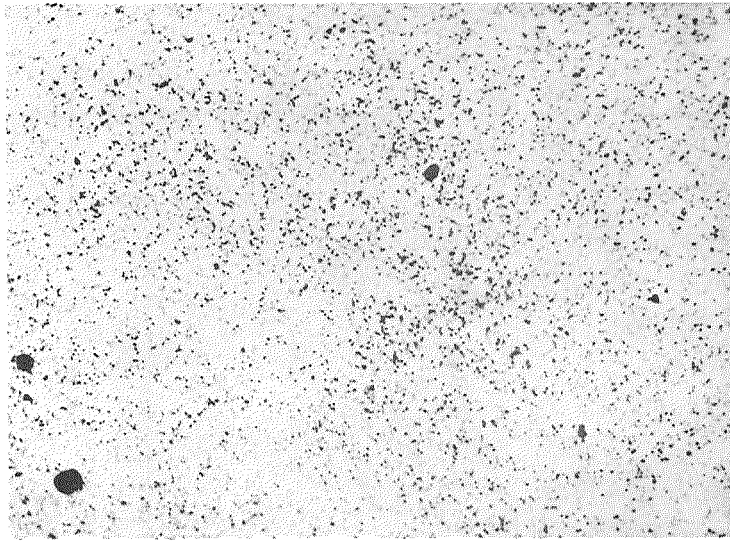


Fig. 5  
B5614

x 500

Structure of the Cr 0.5 wt % Ti 1.14 wt % Be cast No. AA388  
heat treating 15 hours at 2730°F (1500°C).

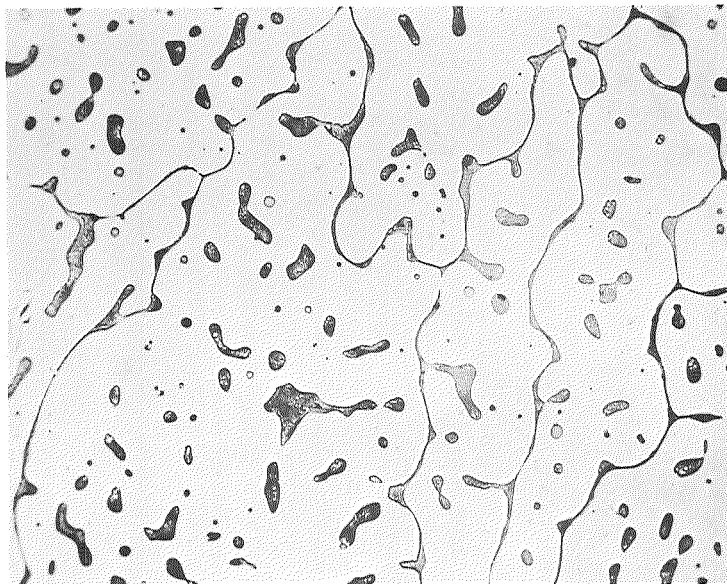


Fig. 6  
F4325

x 250

Structure of Cr 3.80 wt % Zr 0.58 wt % Si Cast No. AA381  
as cast showing eutectic.



Plate B5585  
Alloy AA386  
x 250

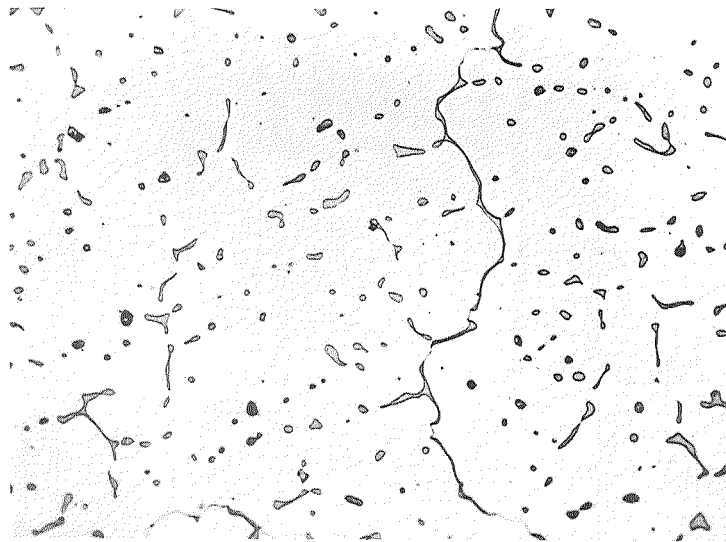


Plate B5624  
Alloy AA386  
x 500

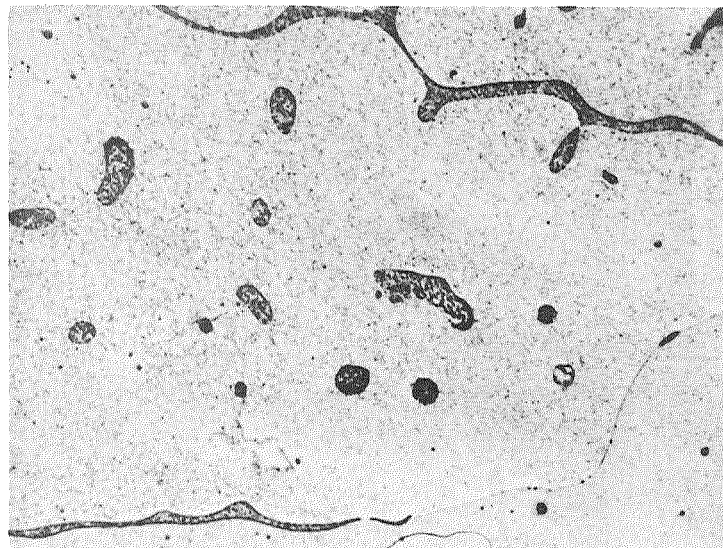


Plate B5611  
Alloy AA385  
x 500

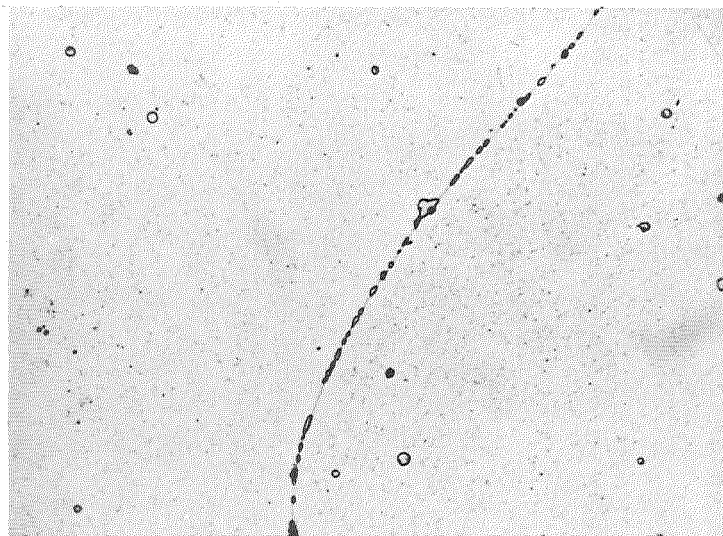
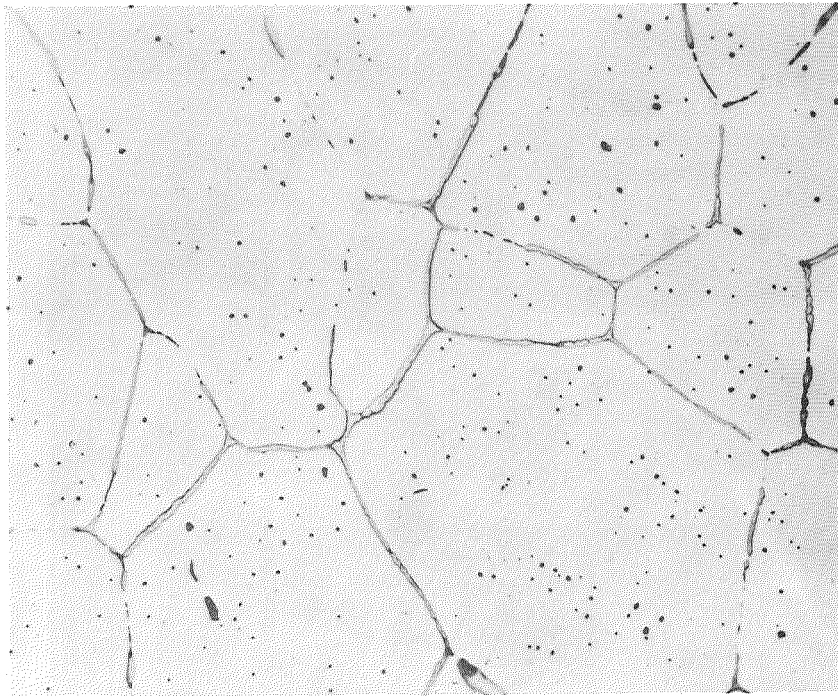


Fig. 7

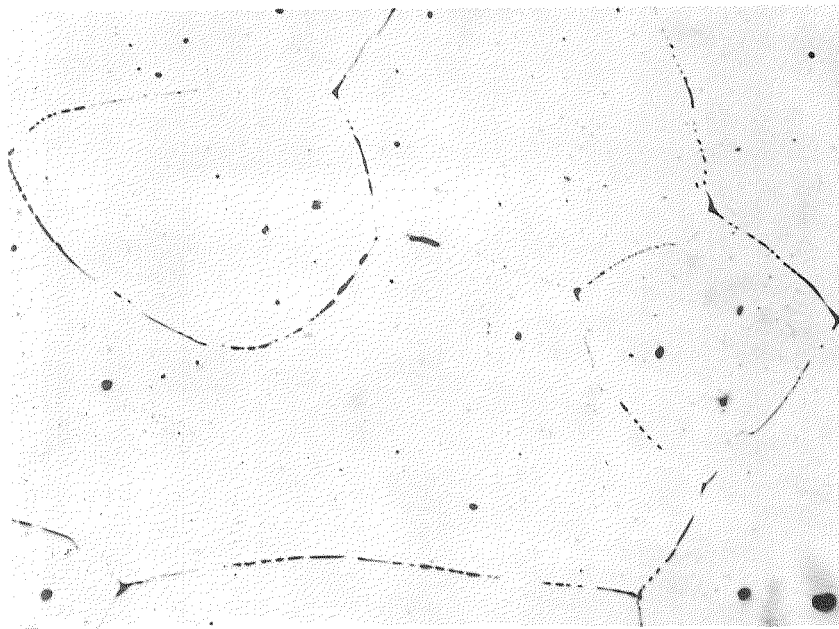
- (a) Structure of Cr 1.2 wt % Zr 1.0 wt % Be alloy AA386 as cast primary compound.
- (b) As (a) after 15 hours 2102°F (1150°C) showing decomposition of primary compound and precipitation.
- (c) Structure of Cr 0.24 wt % Zr 0.20 wt % Be alloy AA385 as cast after 15 hours at 2372°F (1300°C) showing fine intragranular precipitation.



B5759

(a)

X 500



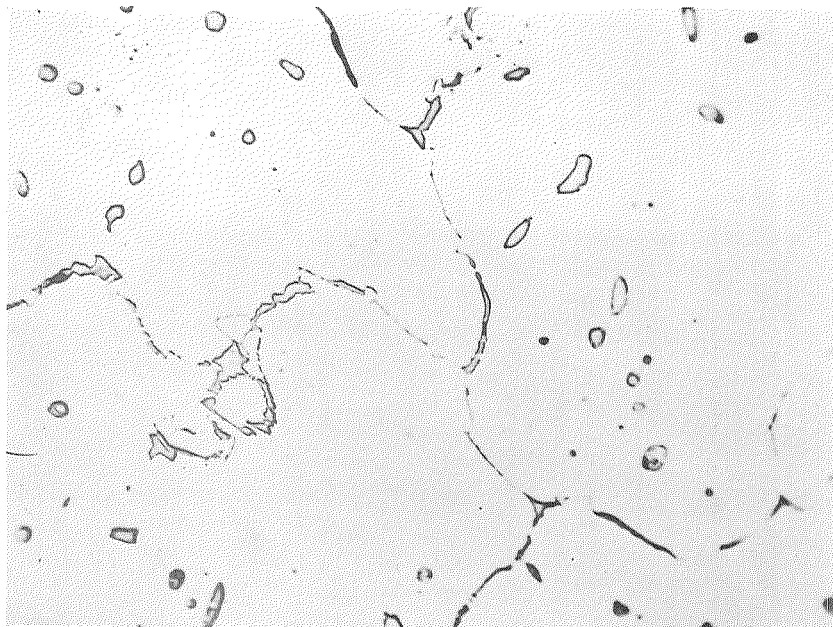
F6798

(b)

X 500

Fig. 8

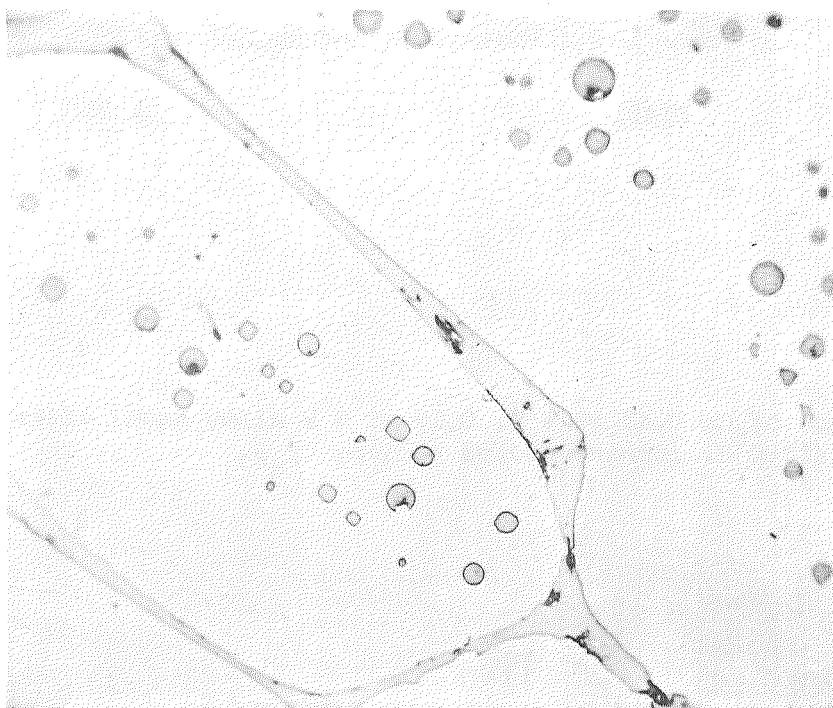
- (a) Structure of Cr 0.55 wt % Ti 0.14 wt % C alloy AA457 showing grain boundary separation of  $\text{Cr}_{23}\text{C}_6$ .
- (b) Structure of Cr 0.83 wt % Ti 0.14 wt % C alloy AA459 as cast.



F 5143

(a)

X 250



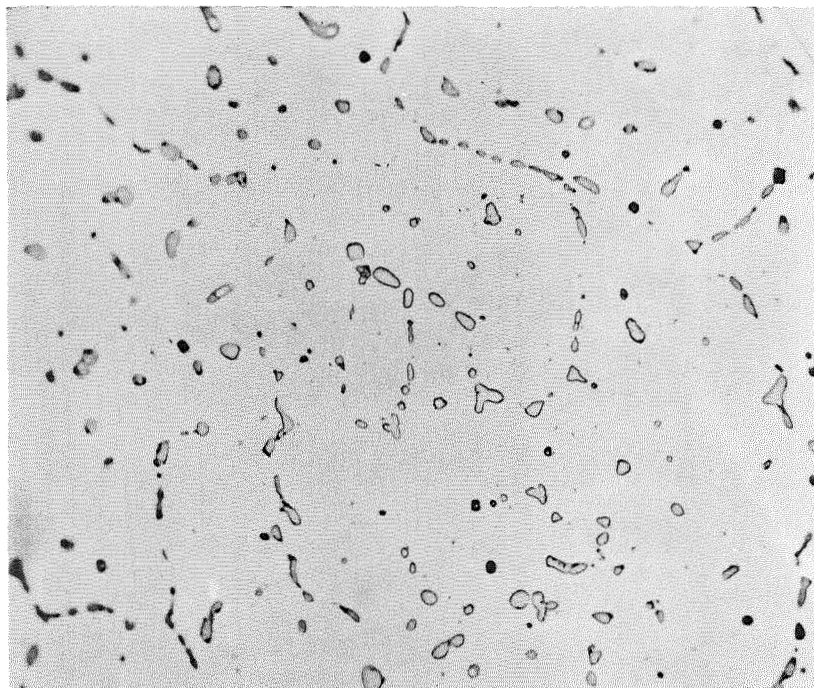
F5493

(b)

X 250

Fig. 9

- (a) Structure of Cr 0.79 wt % Cb 0.19 wt % B alloy AA468 after 25 hours at 2282°F (1250°C) furnace cooled showing Cr<sub>4</sub>B separation.
- (b) As above after 15 hours at 2876°F (1580°C) furnace cooled.



F5491

X 250

Structure of Cr 0.43 wt % Ti 0.19 wt % B alloy AA467 after 22 hours at 2876° F (1580° C) furnace cooled showing  $\text{Cr}_4\text{B}$ .

## APPENDIX

### A.1. Materials

The materials used in this research are as follows:-

#### Chromium

Electrolytic flake produced from a hexavalent bath by the Department of Supply, Melbourne, Australia. Typical limits of impurities are 10 - 230 p.p.m. oxygen; 2 - 10 p.p.m. nitrogen; less than 50 p.p.m. carbon; less than 50 p.p.m. other impurities including metals.

#### Beryllium

Cast and rolled beryllium plate from the Royal Ordinance Factory, Cardiff, U.K. A typical analysis is 99.9% beryllium; 0.08% oxygen; 0.04% iron; 0.04% aluminium; 0.003% carbon; 0.03% nitrogen less than 0.01% other impurities.

#### Columbium

Rod of 99.9% purity supplied by Koch-Light Limited, U.K.

#### Silicon

Transistor grade purity.

#### Titanium and Tantalum

Commercially available metal spraying wire supplied by Metallisation Ltd., U.K.; nominal purity better than 99.9%.

#### Carbon

Spectrographic graphite rod by Johnson Matthey Ltd. U.K.; less than 2 p.p.m. impurities.

#### Boron

Pure boron powder containing not less than 99.99% boron; this was consolidated into pellets before melting.

## A.2. Manufacture

### A.2.1. Melting and Casting

The small 60 gram buttons were prepared in a laboratory argon arc melting and casting furnace; the materials were melted on a water cooled copper hearth, by a D.C. arc from a tungsten electrode in an atmosphere of argon at a pressure of 15 cm of mercury. In operation the furnace chamber was first evacuated to 1 torr and was flushed 3 times with argon of 99.995% purity. The chamber was then filled with argon to a pressure of 15 cm of mercury and this was further purified by gettering with a zirconium button for three minutes. To ensure uniformity of composition, each charge was melted at least three times alternatively on each side of the button. Where the alloy contained small quantities of alloying elements like carbon or boron, master alloys were first prepared by argon arc melting the pure materials with chromium.

The larger 2.75 kg ingots were prepared in a consumable electrode argon arc melting furnace. These melts were prepared in stages. First an electrode was prepared by a non-consumable arc melting process and secondly this electrode was melted and cast to provide the 2½" (6.4 cm) diameter ingot. The first stage comprised the consolidation of the charge by melting it in a water cooled copper trough. Half the chromium was mixed with the alloy constituents until uniform and the mixture was then distributed along the trough, at the end of which was a steel stud; this is welded into the end of the electrode and is necessary for holding the completed electrode in the consumable arc furnace. The trough was evacuated and out-gassed by heating after which it was filled with argon at 15 cm mercury pressure; the charge was then argon arc melted by passing the trough under a tungsten electrode. The latter extended into the furnace by means of a ball and socket joint which allowed movement of the electrode so that the arc could be played over the whole charge to ensure complete melting. The electrode part-formed by this process was then turned over and the rest of the chromium placed uniformly around it. The whole process was then repeated and a satisfactory electrode prepared.

This finished electrode was then transferred to the consumable arc melting furnace. After evacuating the furnace, out-gassing and filling with argon at the correct pressure an arc was struck between the electrode and a piece of chromium placed in the bottom of the 2½" (6.4 cm) diameter water cooled copper crucible. The electrode was then melted and cast into the crucible by appropriately lowering the electrode at a rate commensurate with maintaining a stable arc. The ingots cast in this manner were then machined to 2½" (5.4 cm) diameter for extrusion. Crack testing showed that all ingots were sound.

### A.2.2. Fabrication

These ingots were extruded to  $\frac{1}{2}$ " (1.3 cm) diameter bar on a 100 ton vertical hydraulic press at the National Physical Laboratory, Teddington, England. The ingots were soaked at temperatures of 2370°F (1300°C) to 2550°F (1400°C) in a hydrogen atmosphere prior to extrusion. A glass lubricant was used during extrusion which protected the material from atmospheric attack.

The  $\frac{1}{2}$ " (1.3 cm) diameter bar was rolled to roughly  $\frac{1}{4}$ " (0.64 cm) dia. at Fulmer by the following process. Lengths of the extruded rod were machined to clean any surface imperfections away, then inserted into an appropriate hole in a 1" (2.5 cm) diameter mild steel cylinder. An end plug was then electron beam welded to the cylinder and these sheathed samples were heated at 2120°F (1160°C) and then rolled to give a chromium bar of diameter of  $\frac{1}{4}$ " (0.64 cm).

### A.2.3. Heat Treatment

Heat treatments of samples at temperatures below 2730°F (1500°C) were carried out in a platinum wound tube furnace; for higher temperatures a molybdenum wound furnace was used. All heat treatments were carried out in a hydrogen atmosphere which was purified by diffusion through palladium tubes and the high purity was maintained by gettering with chromium flake samples placed adjacent to the specimens. Temperatures were measured using platinum v platinum-13% rhodium thermocouples at the lower temperatures and platinum 6% rhodium v platinum-30% rhodium couples at the higher temperatures.

## A.3. Experimental Techniques

### A.3.1. Optical Metallography

Samples were mounted in bakelite and were prepared for optical examination by grinding on silicon carbide papers followed by polishing on cloths with chromium sesquioxide and alumina as the abrasives. The alloys containing carbides were also given a final attack polish using a solution of 1% oxalic acid. Specimens were electrolytically etched in either a 10% oxalic acid solution or one containing chromium trioxide and sulphuric acid. (1 gm  $\text{CrO}_3$  2 ml.  $\text{H}_2\text{SO}_4$ , 100 ml water).

### A.3.2. Electron Metallography

Several samples were examined in a Cambridge Instrument Mark I scanning electron microscope containing an electron beam microprobe analysis attachment in an attempt to determine the composition of precipitated phases. A limited amount of electron microscopy of thin films and replicas taken from the surface of the specimens was also carried out using a Siemens electron microscope.

#### A.3.3. X-Ray Diffraction Analysis

The carbide and boride phases were extracted as residues after dissolving the matrix in 10% HCl solution. For the analysis the extracts were mounted in thin walled quartz capillary tubes and exposed in a Philips 11.45 cms diameter Debye-Scherrer camera using either  $\text{CoK}\alpha$  or  $\text{CuK}\alpha$  radiation. Any fluorescent radiation from the specimens was absorbed by a 0.001" (0.0025 cm) nickel filter placed between the specimen and film. The general composition of the matrices was determined from lattice parameter measurements made on sliver specimens approximately 0.010" (0.025 cm) diameter prepared from the heat treated bulk samples. The sliver samples were also exposed in the Philips Debye-Scherrer camera. The compositions were obtained by comparing the measured lattice parameters with published values for the variation in chromium lattice parameter with solute contents.

The precipitates in the intermetallic systems could not be identified by extraction techniques. Those in the zirconium beryllium alloys were however identified from X-ray transmission photographs, from 0.004" (0.01 cm) thick specimens, taken with monochromatic  $\text{MoK}\alpha$  radiation from a quartz crystal focussing monochromator. This technique produces a very low background intensity which is essential for detecting weak diffractions. Precipitate diffractions were observed after 3.0 days exposures at 28kV 6.0 ma. A low excitation potential of 28kV was used so that the beam from the monochromator contained only the characteristic  $\text{MoK}\alpha$  wavelength and none of the sub-harmonic wavelengths.

The texture and worked structure of the extruded and rolled samples were determined from glancing angle X-ray photographs from polished surfaces. These were taken on a Unicam single crystal camera using a cylindrical film cassette.

#### A.3.4. Bend Tests

Bend test specimens, approximately 2" (5.1 cm) long x 0.025" (0.064 cm) wide and 0.046" (0.12 cm) thick, were carefully cut from rolled sheet and electropolished. The specimens were then placed inside a furnace supported on two alumina rods, 1.7" (4.3 cm) apart. The load was applied midway between the rods by a third alumina rod with a V shaped lower end at 0.5 cms/min. The deflection caused by increasing the load and the load applied were plotted on an XY recorder. A thermocouple attached to the specimen recorded its temperature. These tests were used to establish ductile/brittle transition temperatures but as difficulty was experienced in producing rolled sheets for many of the alloys, most of the ductile/brittle transition temperatures were in fact determined using tensile specimens.



#### A.3.5. Tensile Tests

The tensile tests at low temperatures were carried out on a Hounsfield tensometer. The specimens had gauge diameter of 0.18" (.46 cm) and gauge length of 0.632" (1.30 cm); the tests were carried out in air at a nominal strain rate of 0.02 per minute.

The high temperature strength of the alloys was determined using specimens with a gauge length of 1.125" (2.86 cm) and a gauge diameter of 0.16" (.41 cm). These tests were carried out in a special capsule in which the specimen was protected by a slow flow of argon throughout the test. This capsule was fitted to an Instron testing machine and the tests were carried out at a nominal strain rate of 0.03 per minute. The specimens were prepared from the rolled bars using normal turning methods. Each specimen was turned 0.002" over size in diameter; the excess material was removed by electropolishing in a solution of 5% perchloric acid in glacial acetic acid at 6 volts. Visual inspection at a low magnification after polishing revealed cracks in approximately one-third of the specimens; most of these occurred at the specimen shoulders or in the head. Only specimens having their gauge length and shoulders free from cracks were selected for actual testing.

#### A.3.6. Creep Tests

The specimens used for creep testing were the same size as those used for high temperature tests and they were prepared by the same process. The creep tests were carried out in a Denison 1 ton stress rupture machine and the specimens were contained in a special capsule very similar to the one used for high temperature tensile tests.

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